PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : H01M 2/16, D01F 2/00, D04H 1/00, 1/48 | A1

(11) International Publication Number: WO 96/13071

(43) International Publication Date: 2 May 1996 (02.05.96)

(21) International Application Number: PCT/GB95/02474

(22) International Filing Date: 20 October 1995 (20.10.95)

(30) Priority Data:
9421261.0 21 October 1994 (21.10.94) GB

(71) Applicants (*for all designated States except US*): COURTAULDS PLC [GB/GB]; 50 George Street, London W1A 2BB (GB). BONDED FIBRE FABRIC LIMITED [GB/GB]; Bath Road, Bridgwater, Somerset TA6 4NZ (GB).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): KELLY, Andrew, Arthur, James [GB/GB]; Highfields, 22 Silver Street, Wiveliscombe, Somerset TA4 2PA (GB). WOODINGS, Calvin, Roger [GB/GB]; 12 Copsewood Avenue, Nuneaton, Warwickshire CV11 4TQ (GB).

(74) Agent: MANATON, Ross, Timothy; J.Y. & G.W. Johnson, Furnival House, 14-18 High Holborn, London WC1V 6DE (GB).

(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: NON-WOVEN FABRICS FOR BATTERY SEPARATORS COMPRISING A WEB OF SOLVENT-SPUN CELLULOSE FIBERS

(57) Abstract

A non-woven fabric material is described which comprises a dry laid web of solvent-spun cellulose (lyocell) fibers. The material exhibits good strength, wicking properties and stability in alkaline conditions, and is particularly intended for use as a separator in an alkaline battery. Preferred embodiments of material are described, in which the material is bonded, for example by hydroentranglement, the activation of thermally activatable fibers, or the use of a bonding agent. A preferred embodiment of battery separator is also described, which comprises a non-woven material as defined and a membrane of regenerated cellulose film.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

NON-WOVEN FABRICS FOR BATTERY SEPARATORS COMPRISING A WEB OF SOLVENT-SPUN CELLULOSE FIBERS

Field of the invention

This invention concerns non-woven fabrics which can be used, for example, to make battery separators, particularly (but not exclusively) for alkaline batteries.

Background to the invention

The separator for a battery not only performs the function of physically separating the positive and negative electrodes of the battery but it has to contain sufficient of the battery electrolyte to enable the necessary reactions to occur within the battery without significant increases in internal resistance. This requires the separator to be physically strong, have good absorptivity for the electrolyte, and be resistant to attack by the electrolyte (which may, for example, be alkaline). Furthermore, during manufacture of such batteries, it is important for the separators to show rapid wicking of the electrolyte, that is rapid absorption of the electrolyte when electrolyte is applied to one end of a separator. Slow wicking necessitates slowing down of the speed of manufacture of the batteries since substantially complete filling of the separator with electrolyte should occur before further stages of battery manufacture are carried out.

In the past, alkaline battery separators have been made of non-woven materials formed from various types of fibers. Examples of fibers which have been used include natural cellulose, polyolefins, polyesters, polyamides and polyvinyl alcohol. These various fibers have been found to suffer with a variety of disadvantages, natural cellulose fibers tending to have relatively poor stability in alkaline media such as battery electrolytes, and others having relatively poor wicking and/or absorptive properties. Battery separators have therefore frequently been made from natural cellulose fibers, often with other fibers included to improve the mechanical properties of the non-woven material.

The non-woven materials used for prior art battery separators have been made by a variety of processes. One such process for separators made from cellulose fibers is wet laying, which is essentially a paper-making process in which a slurry of randomly oriented natural cellulose fibers, optionally mixed with other fibers if such are desired in the final non-woven material, is dried. If desired, bonding agents, for example polyvinyl alcohol, can be present in the slurry, the bonding agent then serving to give additional strength to the material following drying. Alternatively or additionally, fibers in the slurry can be used to bond the non-woven material, for example by heat activation. For instance, a thermoplastic resin fiber in the material may be heat activated by passing the material through the nip between heated rollers.

EP-A-0572921 describes the production of battery separators by wet laying cellulose fibers obtained by spinning a solution of cellulose in an amine oxide into water. Such solvent-spun fibers have good resistance to the alkaline electrolyte in alkaline batteries compared with natural cellulose fibers. However, when they were wet laid, these fibers did not form a satisfactory non-woven material for a battery separator, apparently due to the high Young's modulus of the fibers when they are wet resulting from the high crystallinity of the cellulose fibers. In order to overcome this problem, it was proposed in EP-A-0572921 to subject the solvent-spun fibers to beating to obtain a highly fibrilated product. Wet laying of these fibrilated fibers apparently facilitates the wet laying process to form a non-woven material which when used as a battery separator inhibits increases in the internal resistance of such batteries.

Summary of the invention

According to one aspect of the present invention there is provided a non-woven material for use as a battery separator, the material comprising a dry laid web of

solvent-spun cellulose fibers. The term generically used for such fibers is "lyocell".

The invention also extends to battery separators comprising such materials, and to batteries including such separators. In an alternative aspect, the invention may be viewed as providing the use of a non-woven material comprising a dry laid web of solvent-spun cellulose fibers as a battery separator.

Description of preferred embodiments

A typical battery (for example an alkaline manganese battery) for which the non-woven materials of the invention are suitable for use as separators comprises a cathode having at least a portion of annular cross-section (which may constitute the casing of the battery), and a cylindrical anode rod disposed generally coaxially within the annular portion of the cathode. The separator in such a battery is formed as a tube, positioned between the anode and cathode. Optionally, one end of the tube may be closed so as to enclose one end of the anode rod; the opposite end of the tube may also be substantially closed, provided that electrical connection is made between the anode and a terminal accessible from the exterior of the battery.

The dry laid lyocell fibers will in general be bonded subsequent to their having been laid. Methods of bonding used hitherto in the art to produce dry laid non-woven materials can be used, for example hydroentanglement, the activation of thermally activatable fibers or the use of a bonding agent applied to the dry laid fibers, for example as a solution.

Non-woven materials in accordance with the present invention have shown particularly rapid wicking when treated with alkaline electrolyte used in alkaline batteries, combined with high levels of electrolyte absorption and resistance to degradation by the electrolyte compared with

hitherto proposed non-woven materials for battery separators. Materials in accordance with the invention have also shown particularly high strength for their weight.

The dry laying of the lyocell fibers can be effected using known methods, it generally being preferred to effect such laying using a carding technique, for example as described in GB 2151667-A. Such carding techniques tend to effect orientation of the carded fibers, with more of the fibers aligned in substantially one direction than in the direction perpendicular thereto. It is generally preferred that the ratio of numbers of fibers aligned generally in one direction to those aligned generally perpendicular thereto is from 2:1 to 10:1, and more preferably from 3:1 to 6:1. The relative numbers of fibers in these directions are preferably selected to provide a balance between increased wicking (with increased alignment) and increased strength perpendicular to the direction in which most of the fibers are aligned.

The thickness of lyocell fibers used in accordance with the present invention can be from 0.5 to 10 decitex, and is preferably from 1 to 3 decitex.

The staple length of lyocell fibers used in accordance with the present invention is preferably from 15 to 60 mm, and more preferably from 30 to 50 mm. This contrasts with the solvent-spun fibers of EP-A-0572921 where the fibers used in the wet laid process are specifically exemplified as being 2 mm long.

Non-woven materials in accordance with the present invention can include fibers other than lyocell fibers, for example fibers which can be used to effect thermal bonding of the non-woven material and/or to increase the resistance of the non-woven material to alkaline electrolyte solutions. Examples of such fibers which can be used include fibers of polyolefins, polyvinyl alcohol, nylons or acrylics. The amount of such other fibers which can be included will

usually depend upon the effect which including them is intended to achieve, but it should not be such as to have a significantly adverse effect on the ability of the material to function in a battery separator.

If desired, the dry laid fibers can be bonded using a bonding agent. A preferred bonding agent is polyvinyl alcohol, preferably in an amount of from 5 to 50 percent by weight, and more preferably 15 to 30 percent by weight, based on the dry weight of the bonded material.

Alternatively, or if desired additionally, the dry laid fibers can be bonded by hydroentanglement, for example as described in EP-A-0147904.

Non-woven materials in accordance with the present invention can be made to a variety of weights per unit area, for example depending on the particular end use. However, typical weights can be 15 to 80 g/m^2, for example 30 to 50 g/m^2.

In general when used to form a battery separator for an alkaline battery, non-woven materials in accordance with the present invention will be used in conjunction with a membrane, for example of regenerated cellulose film.

Unlike the non-woven materials of EP-A-0572921, which require the solvent-spun cellulose fibers to be fibrilated in order to produce a wet laid material, the lyocell fibers used to produce materials in accordance with the present invention can be used in non-fibrilated or fibrilated form. Non-fibrilated fibers are generally preferred since when used in accordance with the present invention they have given good results without the necessity for the extra step of fibrilation of the fibers.

The following Examples are given by way of illustration only.

Example 1

Lyocell fibers of 1.7 decitex and 38 mm length (available from Courtaulds plc, Coventry, United Kingdom, under the trade mark "Tencel") were dry blended with polyvinyl alcohol fibers of 1.4 decitex and 35 mm length at a weight ratio of 60 parts of cellulose fibers to 40 parts of polyvinyl alcohol fibers in a conventional blending and opening process.

Following the blending and opening, the fibers were formed by dry carding into a dry laid web with a weight of 32 g/m². The ratio of numbers of fibers in the machine and transverse directions in the dry laid web was 5:1.

The fibers in the web were then bonded together using an approximately 6% w/v solution of polyvinyl alcohol in water, by first spraying the web with the solution and then drying the web over heated rollers. The weight per unit area and the thickness of the resulting fabric were measured, and the values obtained are shown in the accompanying Table.

The wicking of the fabric was assessed as follows:- A strip of the fabric 14 cm long and 2.5 cm wide (machine direction lengthwise) was clamped so that one end of the fabric was just in a 32 percent by weight aqueous solution of potassium hydroxide. The wicking height was measured as the minimum distance travelled by the solution up the fabric in five minutes. The result is shown in the accompany Table.

The absorbency of the fabric was assessed as follows:- A square or circle of the fabric having an area of 100 cm² was weighed and then placed in a 32 percent by weight solution of potassium hydroxide for one minute. The fabric sample was then removed and allowed to drain for 30 seconds, after which it was reweighed. The increase in weight of the fabric was then expressed as an increase in g/m². The

result is shown in the accompanying Table.

Example 2 (Comparison)

A fabric was produced using the dry laying and bonding method of Example 1 but replacing the lyocell fibers with natural cellulose fibers of substantially the same size as the lyocell fibers.

The test data established for this fabric using the conditions in Example 1 are given in the accompanying Table.

Example 3 (Comparison)

A commercially available wet laid, polyvinyl alcohol bonded cellulose fiber battery separator fabric was subjected to wicking and absorbency tests described in Example 1. Since the cellulose fibers of the fabric had been wet laid, the fibers were essentially randomly oriented. The sample for the wicking test was therefore taken at random from the fabric.

The data obtained for this fabric using the test conditions described in Example 1 are given in the accompanying Table.

Table

Example	Fabric weight (g/m^2)	Thickness (μm)	Wicking (mm/ 5 min)	Absorbency (g/m^2)
1	36	163	44	475
2 (Comparison)	40	178	38	450
3 (Comparison)	50	160	35	400

As can be seen from the data in the above Table, the fabric in accordance with the present invention showed

better wicking and higher absorb ncy than either of the comparison fabrics, and that was for a fabric with a lower weight per unit area than either of the comparison fabrics.

Although the above description concentrates on the use of the materials of the invention in alkaline environments, it is also envisaged that they will find use in acidic and neutral conditions.

CLAIMS

1. A non-woven material for use as a battery separator, the material comprising a dry laid web of solvent-spun cellulose (lyocell) fibers.

2. A non-woven material according to claim 1, wherein the fibers have been hydroentangled subsequent to dry laying.

3. A non-woven material according to claim 1, wherein the fibers have been bonded with a bonding agent subsequent to dry laying.

4. A non-woven material according to claim 3, wherein the bonding has been effected using a binding agent or by heat activatable fibers.

5. A non-woven material according to any of the preceding claims, wherein the dry laid web has a preponderance of fibers aligned in substantially one direction with a minor amount of fibers aligned substantially perpendicular thereto.

6. A non-woven material according to claim 5, wherein the ratio of numbers of fibers aligned in substantially perpendicular directions is from 2:1 to 10:1.

7. A non-woven material according to claim 6, wherein the ratio is from 3:1 to 6:1.

8. A non-woven material according to any of the preceding claims, wherein the solvent-spun cellulose fibers are of from 0.5 to 10 decitex.

9. A non-woven material according to claim 8, wherein the fibers are of from 1 to 3 decitex.

10. A non-woven material according to any of the

preceding claims, wherein the fibers have a staple length of from 15 to 80 mm.

11. A non-woven material according to claim 10, wherein the fibers have a staple length of from 30 to 50 mm.

12. A non-woven material according to claim 3, wherein the bonding agent comprises 5 to 50 percent by weight of the bonded material.

13. A non-woven material according to any of the preceding claims, wherein the solvent-spun cellulose fibers have not been fibrilated.

14. A non-woven material according to any preceding claim, for use as a battery separator in an alkaline battery.

15. A non-woven material according to any of claims 1 to 13, for use in an alkaline manganese battery.

16. A battery separator comprising a non-woven material according to any of the preceding claims.

17. A battery separator according to claim 16, wherein the separator comprises the non-woven material and a membrane of regenerated cellulose film.

18. A battery separator according to claim 16 or claim 17, wherein the separator comprises a tube of said non-woven material.

19. A battery separator according to claim 18, wherein the tube of non-woven material is closed at at least one end.

20. A battery including a battery separator according to any of claims 16 to 19.

21. An alkaline battery including a battery separator according to any of claims 16 to 19.

22. An alkaline manganese battery including a battery separator according to any of claims 16 to 19.

23. The use of a non-woven material comprising a dry laid web of solvent-spun cellulose (lyocell) fibers as a battery separator.

24. The use according to claim 23, in which the battery is an alkaline battery.

25. The use according to claim 24, in which the battery is an alkaline manganese battery.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 95/02474

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01M2/16 D01F2/00 D04H1/00 D04H1/48

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01M D01F D04H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP-A-0 521 444 (JAPAN VILENE CO LTD) 7 January 1993 see page 1, line 5-7 see page 1, line 47-51 see page 8, line 33-36 ---	1-25
Y	EP-A-0 572 921 (KURARAY CO ;MATSUSHITA ELECTRIC IND CO LTD (JP)) 8 December 1993 cited in the application see page 4, line 7 - page 5, line 21 see page 7, line 18-21 see example 1 see claims 1-11 --- -/--	1-25

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 March 1996	02.04.96

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Engl, H

International Application No
PCT/GB 95/02474

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 008 no. 111 (E-246) ,24 May 1984 & JP,A,59 025164 (HIROYUKI KANAI) 9 February 1984, see abstract ---	
A	EP-A-0 503 811 (DEXTER CORP) 16 September 1992 see the whole document -----	

2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 95/02474

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0521444	07-01-93	JP-A-	5009813	19-01-93
		JP-A-	5163649	29-06-93
		JP-A-	5177133	20-07-93
		KR-B-	9406859	28-07-94
		US-A-	5430911	11-07-95
		US-A-	5375298	27-12-94
EP-A-0572921	08-12-93	AU-B-	3983593	02-12-93
		CA-A-	2097405	02-12-93
		CN-A-	1083973	16-03-94
		JP-A-	6163024	10-06-94
		US-A-	5366832	22-11-94
EP-A-0503811	16-09-92	US-A-	5158844	27-10-92
		AU-B-	640264	19-08-93
		AU-B-	8344191	17-09-92
		CA-A-	2045076	08-09-92
		JP-A-	4312763	04-11-92